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Export of anthropogenic reactive nitrogen and sulfur compounds from the East Asia region in spring

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Abstract. Measurements of gaseous and particulate compounds of reactive nitrogen and sulfur species, as well as other chemical species, were made using the P-3B and DC-8 aircraft over the western Pacific during the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) experiment, conducted between February and April 2001. These measurements provide a good opportunity to study the extent to which anthropogenic NO_x and SO_2 emitted over the East Asian countries remain as NO_y and SO_x (= SO_2+nssSO_4^{2-}), when an air mass is transported into western Pacific region. In this paper, a method to estimate the transport efficiencies, $\varepsilon(NO_y)$ and $\varepsilon(SO_x)$, in an air mass that has experienced multiple injection, mixing, and loss processes is described. In this analysis, CO and CO_2 are used as passive tracers of transport, and the emission inventories of CO, CO_2, NO_x, and SO_2 over the East Asia region are used. The results from the P-3B presented in this study indicate that 20-40% and 15% of NO_x emitted over the northeastern part of China remained as NO_y over the western Pacific in the boundary layer (BL) and free troposphere (FT), respectively. PAN is found to have been the dominant form of NO_y, while only 0.5% of emitted NO_x remained as NO_x in the FT. The transport efficiency of SO_x is estimated to have been 25-45% and 15-20% in the BL and FT, respectively. Median values of the nssSO_4^{2-}/SO_x ratio are 0.4-0.6 both in the BL and FT, however large variability is found in the FT. These results are generally consistent with those derived using DC-8 data. The results obtained in this study indicate that more than half of NO_y and SO_x were lost over the continent and that the vertical transport from the BL to FT further reduced their amounts by a factor of 2 likely due to wet removal. Budgets of NO_y and SO_x are also studied and the total flux out from the continent is estimated to be 20% of the emissions. Flux in the BL and FT is found to have a similar contribution.

1. Introduction

Anthropogenic emissions of nitrogen oxides (NO_x = NO + NO_2) and sulfur dioxide (SO_2) in East Asian countries are of great concern because of their impact on the atmospheric environment on regional and intercontinental scales. These two compounds play critical roles in controlling the oxidizing power of the atmosphere and air quality, causing acid rain, and changing radiative forcing, through gas-phase chemistry and particle formation. Rapid economic growth and increasing fossil fuel energy consumption in the People's Republic of China in the past two decades has resulted in large emissions of reactive nitrogen and sulfur compounds into the atmosphere. China is expected to undergo further economic growth and modernization in the next several decades. Emissions of SO_2 from China, however, are estimated to have reached a peak level in 1996, followed by a slow decline, due to a combination of environment regulations and other factors, although the primary energy source still relies on coal burning [*Streets et al*, 2000; *Streets et al*, this issue]. Emissions of NO_x due to commercial energy use in China are also estimated to have been the greatest in 1996, with a subsequent declining trend, mainly due to the reduction of coal consumption [*Hao et al*., 2002]. Consequently, future emissions of NO_x and SO_2 from China will be less than those anticipated in the early to mid-1990s. Nevertheless, current emissions from China are still large and dominant in Asia for NO_x (42%) and SO_2 (59%) [*Streets et al*, this issue], and a further increase in NO_x emissions is anticipated in Southeast Asia and the Indian subcontinent [*van Aardenne, et al*, 1999].

Anthropogenic emissions of NO_x and SO_2 occur predominantly at the continental surface, and chemical conversion and loss processes take place within the boundary layer. Eventually these air masses leave the source region via horizontal transport within the boundary layer and free troposphere. The concentrations in the free troposphere are smaller than in the boundary layer because a large fraction of the species is removed in the boundary layer before transported to the free troposphere.

Soluble species can be removed further by wet deposition during vertical transport resulting influences from anthropogenic emissions smaller in the free troposphere. Horizontal transport in the free troposphere however, is efficient for long-range transport due to an increasing westerly wind speed with altitude. Processes of transport and the regional budget of anthropogenic reactive nitrogen and sulfur compounds over the East Asia region have been studied by many investigators using three-dimensional model simulations [e.g. *Bey et al*., 2001; *Xiao et al*., 1997; *Chin et al*., 2000; *Tan et al.*, 2002]. In these studies, observations, such as aircraft measurements made during the Pacific Exploratory Mission in the Western Pacific Ocean (PEM-West), were used to evaluate the validity of the model calculations. However, measurements, which can be used for quantitative evaluation, are still limited.

Measurements of gaseous and particulate compounds of reactive nitrogen and sulfur species, as well as other chemical species, were made from the NASA P-3B and DC-8 aircraft over the western Pacific during the NASA Transport and Chemical Evolution over the Pacific (TRACE-P) experiment, conducted between February and April 2001. The major goal of the TRACE-P experiment is to evaluate the impact of outflow from Asia, especially that of anthropogenic emissions over the Asian continent, on the atmospheric environment.

During the TRACE-P experiment, we occasionally sampled air masses that had been influenced by anthropogenic emissions over China and other East Asian countries. Using these data, we estimate in this study the extent to which anthropogenically emitted reactive nitrogen and sulfur compounds were transported from the continent into the western Pacific region, using CO and CO_2 as passive tracers. For this purpose, background levels of CO, SO_x (= SO_2+nssSO_4^{2-}), and NO_y are estimated for individual air masses, and increases of these species above their background levels, ΔCO, ΔSO_x, and ΔNO_y, are calculated. Ratios of increases, $\Delta SO_x/\Delta CO$ and $\Delta NO_y/\Delta CO$ are then compared with emission ratios E_{SO2}/E_{CO} and E_{NOx}/E_{CO}. We define transport efficiency

$\varepsilon(NO_y)$ and $\varepsilon(SO_x)$, as follows.

$$\varepsilon(NO_y) = \Delta NO_y / [\Delta CO \times E_{NOx} / E_{CO}] \quad (1)$$

$$\varepsilon(SO_x) = \Delta(SO_2 + nssSO_4^{2-}) / [\Delta CO \times E_{SO2} / E_{CO}] \quad (2)$$

The denominators are the expected increase in NO_y or SO_x deduced from the observed ΔCO value, while the numerators are the observed increases, ΔNO_y or ΔSO_x. In this paper, a method to estimate the transport efficiencies, $\varepsilon(NO_y)$ and $\varepsilon(SO_x)$, in an air mass that has experienced multiple injection, mixing, and loss processes, is described. Vertical profiles of $\varepsilon(NO_y)$ and $\varepsilon(SO_x)$ are presented and possible processes resulting these efficiencies are discussed. Most of the analyses are made using the P-3B data set because NO_y measurements are available. The DC-8 data set is used to compare the results from the two platforms to confirm the results from the P-3B.

2. Measurements

In this study, gas and aerosol data obtained on board the NASA P-3B and DC-8 aircraft were used. Techniques used for these measurements are listed in Table 1, as well as their references.

The treatment of aerosol measurements is briefly described here. In the measurements of NO_y onboard the P-3B, NO_y compounds were catalytically converted to NO on the surface of a heated gold tube with the addition of CO, and NO was subsequently detected by an NO-O_3 chemiluminescence technique [*Kondo et al*., 1997; *Koike et al*., 2002]. Although the inlet tube for air sampling faced rearward, particles with diameters smaller than about 1 μm are considered to have been sampled by the NO_y instrument. Because of the operating temperature of the NO_y converter (300°C), ammonium nitrate (NH_4NO_3, boiling point 210°C) would be expected to thermally dissociate, while sodium nitrate ($NaNO_3$, boiling point 380°C) and calcium nitrate ($Ca(NO_3)_2$, melting point 561°C) would not be converted.

Aerosol particle chemical composition, such as sulfate (SO_4^{2-}) and nitrate (NO_3^-), were measured onboard the P-3B, using a particle-into-liquid sampler (PILS) [*Weber et al*., 2001]. The collection efficiency of particles with diameters smaller than 0.7 μm was estimated to be about 90%, decreasing to 50% for particles with diameters of 1.2 μm. The efficiency for particles larger than 3 μm in diameter was negligible. This collection efficiency was similar to that of the NO_y instrument, and both instruments are considered to sample particles in a similar size range.

Sulfate aerosol measurements onboard DC-8 were made using a mist chamber and ion chromatography (MC-IC) technique. The median upper particle size cutoff was estimated to be 2.7 μm in diameter. Because of this larger cutoff size as compared with that of the PILS instrument, a greater number of coarse mode dust particles including calcium sulfate ($CaSO_4$), is expected to have been sampled. During the three P-3B/DC-8 intercomparison flights made during TRACE-P, agreements within 30-50%

were found between P-3B/PILS and DC-8/MC-IC SO_4^{2-} measurements [*Ma et al.*, 2002]. The MC-IC values were systematically lower during one of the intercomparison flights in spite of larger cutoff size, suggesting that the observed differences were resulted from the error in the measurements.

For the P-3B data set, amounts of non-sea-salt sulfate ($nssSO_4^{2-}$) were calculated from measurements of SO_4^{2-} and Na^+ using an empirical relationship in seawater. Because Na^+ data in the MC-IC SO_4^{2-} size range is not available for the DC-8 data set, SO_4^{2-} values are used as $nssSO_4^{2-}$ values. In this study, we denote SO_2+$nssSO_4^{2-}$ as SO_x, which is considered to be a product of anthropogenic SO_2 emissions.

For analyses using the P-3B data set, all data were averaged to the aerosol-sampling time interval of about 3 minutes. For analyses using the DC-8 data set, all data were averaged for the mist chamber sampling time interval of about 1 minute.

3. Study Area and Emission Data

3.1. Study Area

Figure 1 shows the flight tracks of the NASA/P-3B aircraft during TRACE-P. Five-day kinematic back trajectories of air masses sampled from the P-3B were calculated using the method described by *Yamanouchi et al*. [2002], with meteorological data provided by the European Centre for Medium-Range Weather Forecasts (ECMWF) on a 1º ×1º latitude-longitude grid. Using these trajectories, we defined the study area as 30°N-42°N and 124°E-140°E for the present study. A latitudinal boundary of 30°N was chosen because back trajectories of air masses sampled south of 30°N (17°N-30°N) passed over Southeast Asia, where hot spots due to biomass burning were frequently observed by the Advanced Very High Resolution Radiometer (AVHRR) satellite instrument during the TRACE-P period. In fact, air masses likely influenced by biomass burning (high CH_3Cl and K^+ concentrations) were occasionally observed at these latitudes in the free troposphere. A longitudinal boundary of 140°E was chosen, because a volcano on Miyakejima Island (34°N, 139°E) was quite active during the TRACE-P period, and a huge amount of SO_2 was likely emitted from it. Furthermore, air masses, which could have been influenced by the Miyakejima Island volcano, were discarded based on back trajectory analysis. Almost all of the air masses sampled in the study area were transported from over the continent at latitudes between 30°N-60°N by predominant westerly flow [*Fuelberg et al*., this issue]. These air masses are expected to have been influenced by anthropogenic emissions over the continent, and we therefore denoted air masses sampled in the study area as "continental air masses." They were sampled during five flights (NASA/P-3B flight 13, 14, 16, 18, and 19) made between March 17 and April 2.

Emission ratios of CO, CO_2, NO_x, and SO_x (described in the next section) in Japan and the Republic of Korea (South Korea) are different from those in China. We thus further distinguished "Chinese air masses" from "continental air masses" using back

trajectories. "Chinese air masses" are defined as those that passed over China at altitudes below the 800-hPa level (boundary layer) within 5 days prior to the measurements. We excluded air masses of Chinese origin that passed over South Korea and/or Japan at altitudes below 800 hPa. Locations where "Chinese air masses" were sampled are shown in Figure 1. They are a sub-group of "continental air masses" and will be used to confirm the results of the influences from China derived using "continental air masses."

3.2. Emission Data

A comprehensive inventory of air pollutant emissions in Asia was developed for the year 2000 [*Streets et al*., this issue]. For this estimate, all major contributing sources, such as power plants (coal and oil), transportation (oil), industrial sources (coal and oil), domestic sources (coal and biofuel), and biomass burning were taken into account. Because emissions of various species were calculated from the common model of activity rate (e.g., fossil fuel energy use rate), these estimates are considered to be internally consistent. In general, other emission estimates were made in less consistent ways, as different investigators use different models for different species. The consistency of emission estimates is important in the present study, because we estimated the transport efficiency using emission ratio information, as shown in equations (1) and (2).

In this study, emission data for CO, CO_2, NO_x, and SO_2 were used. Figure 2 shows the emissions of these species in the East Asian countries in the year 2000. High-emission regions are generally located in the coastal area of the northeastern part of China, Japan, and South Korea. Annual emissions from China were estimated to be 4.13 tera-mol (Tmol) for CO, 86.7 Tmol for CO_2, 0.247 Tmol for NO_x, and 0.318 Tmol for SO_2 with a 95% confidence level of 156%, 16%, 23%, and 13%, respectively [*Streets et al*., this issue]. Uncertainty is greatest for CO, because emission factors are

highly dependent on the efficiency of the combustion process. In fact, a comparison of model calculations using this emission inventory with observations suggests that CO estimates for China are low [*Palmer et al*., this issue; *Carmichael et al*., this issue]. It is noted that although annual average emission rates are used in this study, emissions in March (TRACE-P period) are close to the annual averages [*Streets et al*., this issue].

In Figures 3a-3c, the correlation between the emission rates of CO, CO_2, NO_x, and SO_2 in China within the region of 25°N-50°N and 100°E-130°E (except for the South Korea region) is shown using gridded emission data with a spatial resolution of 1° x 1°. This region was chosen because most of the air masses sampled in the study area (30°N-42°N and 124°E-140°E) were transported through this region. As seen in these figures, emission rates assigned to each grid point show positive correlations with CO emissions. A correlation coefficient is slightly better when CO_2 is used instead of using CO as a reference gas; r^2 value for NO_x-CO_2 and SO_x-CO_2 is 0.96 and 0.82, respectively. These good correlations are unexpected because the emission ratios E_{CO}/E_{CO2}, E_{NOx}/E_{CO}, and E_{SO2}/E_{CO} in China are actually quite different for different emission sources. For example, coal-fired power plants are the largest source for SO_2 and NO_x in China, though CO emission from this source is negligible [*Streets et al*., this issue]. It is likely that large sources of CO (such as transportation) are co-located with these power plants and a relatively good correlation has resulted. Our method to estimate the transport efficiency defined by equations (1) and (2) requires the same emission ratio be used for all air masses influenced by local emissions at different locations. Further refinements of the emission database should indicate whether the assumption can be justified.

Total emissions in the region of 25°N-50°N and 100°E-130°E, except for emissions from South Korea, are given in Table 2. They correspond to about 70% of the total emissions from China. In Table 2, ratios of these total amounts are also given and are shown using solid lines in Figures 3a-3c. We used these values as E_{CO}/E_{CO2},

E_{NOx}/E_{CO}, and E_{SO2}/E_{CO} ratios in the following analyses. Because the boundaries of the region for the emission statistics were chosen to be well away from the locations of highest emissions, the emission ratios are not sensitive to the choice of boundary locations.

4. Approach

4.1. Estimation of Transport Efficiency

As described in section 1, the transport efficiency of anthropogenically emitted reactive nitrogen and sulfur compounds, defined in equations (1) and (2), was estimated in the present study. For this purpose, background levels of CO, CO_2, NO_y, and SO_x were determined for individual sampled air masses, instead of using common values for all air masses. The definition of the "background value" of an air mass in this study is the value, which an air mass would have had if it had not been influenced by anthropogenic sources in the East Asian countries.

To describe our approach to the transport efficiency estimation, an example of the CO-CO_2 relationship is shown in Figure 4a. We made two simple assumptions. First, CO and CO_2 values in background air masses have a linear relationship. Second, the ratio of increases of CO to CO_2 due to anthropogenic emissions is always the same and can be expressed by an emission ratio, E_{CO} / E_{CO2}, derived from the emission inventories. An argument for the validity of the first assumption is described in the next section. The second assumption is supported by the relatively good correlation between emissions of CO and CO_2 shown in Figure 3a. In addition, we assumed the loss of CO and CO_2 is negligible. Because air masses were sampled in our study area only 0 to 5 days after leaving the continent, this assumption is also reasonable.

In Figure 4a, A and B are background air masses, and a line connecting them shows the background linear relationship. Let us assume an air mass C is produced by the mixing of A and B. Air mass C can also be considered as a background air mass, because it is not affected by anthropogenic emissions. Now let us assume another case in which both air masses A and B receive emissions (denoted A' and B'). The slopes between A and A' and between B and B' are equal to the emission ratio, E_{CO} / E_{CO2}. Consider that air mass C' is produced by the mixing of A' and B' with the same ratio of mixing as when C is produced from A and B. The difference between C and C' can be

considered as the influence of anthropogenic emissions. The slope between C and C' is thus equal to the emission ratio E_{CO}/E_{CO2}. Consequently, once C' is obtained from observations, the background value C can be calculated for this particular air mass using the emission ratio E_{CO}/E_{CO2} and the background relationship. Values of ΔCO and ΔCO_2 can then be calculated from the difference between values in air masses C and C'. Note that the resulting air mass C' can be interpreted as resulting from a single injection of CO and CO_2 with an E_{CO}/E_{CO2} ratio into air mass C. Because of the linearity of the mixing process, a unique background value can be determined for an air mass that has experienced multiple mixing and multiple injection processes.

The method to calculate the transport efficiency of NO_y is now described using Figure 4b. We assume again that NO_y and CO values in background air mass have a linear relationship and that a ratio of enhancement following emissions can be expressed by an emission ratio, E_{NOx}/E_{CO}. Because we know the ΔCO value for this air mass from the CO-CO_2 correlation (Figure 4a), we can calculate a background value of NO_y (NO_y value in air mass C). The expected NO_y value due to inputs of anthropogenic emissions (NO_y value in air mass *expected* C' in Figure 4b) can then be calculated using E_{NOx}/E_{CO}. The measured NO_y would have been at this expected NO_y value if NO_y were to behave as a passive tracer. The observed NO_y value (NO_y value in air mass C'), however, can be lower than the value in air mass *expected* C', because of the loss of NO_y. The ΔNO_y value is defined by the difference between the observed value (C') and background value (C). When ΔNO_y is divided by the expected increase in NO_y (the difference between C and *expected* C'), one can easily derive an equation (1), and the transport efficiency of NO_y, $\varepsilon(NO_y)$, can be calculated. Note that the NO_y value in an observed air mass can be even lower than the "background relationship line" in the NO_y-CO diagram, as shown as an air mass C'' in Figure 4b. Even in this case, the ΔNO_y value is still positive when the background value of this air mass (C) is lower than the observed value C''.

In the same way, the transport efficiency of SO_x, $\varepsilon(SO_x)$, can be calculated. Note that if CO_2 is used as a reference gas to calculate the transport efficiency defined by equations (1) and (2) instead of using CO, the same result is obtained. This is because ΔCO and ΔCO_2 are interconnected as $\Delta CO/\Delta CO_2 = E_{CO}/E_{CO2}$.

In our approach we assume the background relationship does not change, even when a loss of NO_y or SO_x takes place and a decrease in NO_y or SO_x (the difference between *expected*-C' and C') is attributed to a loss within anthropogenically injected NO_y or SO_x. In reality, however, NO_y or SO_x molecules, which originally belong to background air masses, are also lost during a loss process. Consequently, the transport efficiency estimated by this approach is considered a lower limit. In the case of $\varepsilon(NO_y)$ estimation, lightning NO production and aircraft emissions can cause an overestimation and these effects will be addressed in section 5.7.

An advantage of this method is that it can be used under the condition of multiple mixing, multiple injection, and multiple loss processes. Although we cannot tell when NO_y or SO_x is lost, we can calculate the fraction of net loss. The first key to this method is that instead of using a single value of CO or CO_2 as the background, we use a linear relationship between CO and CO_2 in background air masses, which covers certain ranges of CO and CO_2, to derive ΔCO. The other key is the use of emission ratios to estimate background values. In the next section, a determination of the background relationships is described.

4.2. Background Relationships

In Figures 5a-5d, vertical profiles of CO, CO_2, NO_y, and SO_x (= SO_2+nssSO_4^{2-}) observed from the P-3B aircraft are plotted using potential temperature as the vertical coordinate. For these figures, all data points obtained at west of 155°E are used irrespective of the latitude (17°N-42°N) except for those possibly influenced by a volcano on Miyakejima Island. Minimum values of CO, CO_2, and NO_y at each

potential temperature level change smoothly with potential temperature. The solid line in each figure is a polynomial fit calculated for minimum values at each potential temperature level, and they will be referred to as "minimum value lines." Considering the fact that all of the air masses sampled in our study area had been transported from the Asian continent, these minimum values suggest the background levels of these species. Note that the minimum value at each potential temperature surface changes little with latitude. When geometric altitude is used instead of potential temperature, the minimum values change with latitude because of air mass motions along isentropic surfaces [*Koike et al*., 1997]. In the case of SO_x, the background level was suggested to be close to zero, because very low concentrations were frequently observed.

In Figure 6a, a scatter plot between CO and CO_2 is shown using "continental air mass" data. In this plot, the color was coded using the altitude at which the air mass was sampled. From Figures 5a and 5b, pairs of CO and CO_2 values on the "minimum value lines" were calculated at various potential temperature levels between 280 and 310 K (open squares in Figures 5a and 5b), and they are also plotted in Figure 6a using open squares. As seen in this figure, these "minimum values" are linearly correlated within this CO and CO_2 range. Considering the fact that these "minimum values" suggest the background levels of CO and CO_2, we use this relationship as the "background relationship" between CO and CO_2.

As seen in Figure 6a, many data points are distributed around the "background relationship" line. Vertical profiles of CO and CO_2 suggest that these air masses have chemical characteristics of a background air mass, which is influenced little by anthropogenic sources over the East Asia. This is further confirmed using a correlation with Halon 1211 and OCS as described below. In Figures 6b and 6c, scatter plots between CO and CO_2 are shown and levels of Halon 1211 and OCS are used for color-coding. Halon 1211 is considered to be a unique tracer for Chinese urban emissions [*Blake et al*., 2001], because China is currently responsible for about

90% of the world's production following regulation by the Montreal Protocol [*Fraser et al*., 1999]. It is used in fire extinguishers and its residence time in the atmosphere is 10 to 20 years. OCS has also been found to be a good indicator of anthropogenic emission from China and likely originates from coal burning (*Green et al*., manuscript in preparation). Coal combustion is a dominant contributor to both CO_2 and SO_2 emission in China [*Streets et al*., this issue]. The global average residence time of OCS was estimated to be about 4 years [*Chin and Davis*, 1995]. As seen in Figures 6b and 6c, both Halon 1211 and OCS values in air masses above the "background relationship" are systematically higher than those in air masses around the "background relationship." This result indicates that air masses around the "background relationship" were influenced little by anthropogenic emissions over China.

In summary, the "background relationship" between CO and CO_2 shown in Figure 6a was established using the minimum values at each potential temperature level observed in our study area. The correlations with both Halon 1211 and OCS confirm the validity of the use of this relationship as the background relationship. In this study, one common "background relationship" is defined for the boundary layer air and free tropospheric air. Thus, transport efficiency can be calculated even when an air masses in the boundary layer and free troposphere are mixed together. The degree of influence from anthropogenic emissions can be estimated by the value of ΔCO, irrespective of the altitude.

The "background relationship" between NO_y and CO was calculated in the same way, using "minimum value lines" shown in Figures 5a and 5c. This relationship is shown as a solid line in a scatter plot between NO_y and CO (Figure 7a). Black squares in this figure denote low-ΔCO air masses ($\Delta CO < 30$ ppbv) in which CO and CO_2 values are close to the CO-CO_2 background relationship line. As seen in this figure, most of the low-ΔCO data correspond to data points around the "background relationship" between NO_y and CO, although some low-altitude data show clear

increases in NO_y. Consequently, the method to estimate the transport efficiency described in the previous section can be applied to NO_y. In the case of SO_x, the background level was chosen to be zero, as described above. However, there is a positive correlation between SO_x and CO in low-ΔCO air masses, and mixing with background air masses could result in some errors in our estimation (Figure 7b). We note that ΔCO values are estimated more accurately than ΔNO_y and ΔSO_x values in this study. The accuracy of the background level determination is more important for CO because the relative variability in CO due to anthropogenic emissions is smaller as compared with that in NO_y [*Parrish et al*., 1991; *Stohl et al*., 2002].

5. Results and Discussion

5.1. Episodes of High-ΔCO Events

In the statistical analyses described in the following sections, we only used air masses in which ΔCO values were greater than 30 ppbv (i.e., air masses clearly influenced by anthropogenic sources over the continent). A threshold value of 30 ppbv was subjectively chosen by assuming a symmetrical distribution of ΔCO values in background air masses around the ΔCO = 0 line ("background relationship" line in Figures 6a-6c). Air masses in which ΔCO > 30 ppbv consisted of 30% of "continental air masses," and this fraction is higher at 0-2 km as compared with that at 2-7 km. Locations where these air masses were sampled are shown in Figure 1. After this selection, 19-42 and 9-29 data points remain in the 0-1, 1-2, and 2-4 km altitude ranges in "continental" and "Chinese" air masses, respectively, while only 2 and 1 data points remain in these two air masses in the 4-7 km range. Results at 4-7 km likely do not represent the average in the western Pacific region.

5.2. Correlation

In Figure 7a, a scatter plot between CO and NO_y is shown using all of the "continental air mass" data. As seen in this figure, enhancements in NO_y are positively correlated with those in CO, suggesting that these NO_y enhancements were due to anthropogenic emissions. The enhancement was greatest at altitudes below 2 km. A clear positive correlation between NO_y and CO, suggesting anthropogenic influences, was also found in the lower and middle troposphere over the western Pacific in February-April 1994, during PEM-West B [*Koike et al*., 1997].

In Figure 7c, a scatter plot between ΔNO_y and ΔCO is shown for "continental air mass" data. The relationship between ΔNO_y and ΔCO is similar to that between NO_y and CO (Figure 7a), because background values of individual data are not very different. Values of ΔNO_y and ΔCO show positive correlation, however, the slope is lower than

the emission ratio, suggesting that anthropogenically emitted nitrogen compounds had been removed from the air masses before they were sampled from the P3-B aircraft. Ratios of increases, $\Delta NO_y/\Delta CO$, are generally higher at altitudes below 2 km as compared to those at higher altitudes, suggesting removal of NO_y during the vertical transport. On the other hand, ratios of increases in air masses in which ΔNO_y and ΔCO values are very high ($\Delta NO_y > 6$ ppbv and $\Delta CO > 400$ ppbv) are similar to those of other air masses. These air masses are considered to have been influenced by anthropogenic sources more strongly, however the removal rate is similar to those of less-influenced air masses.

In Figure 7b, a scatter plot between CO and SO_x is shown using "continental air mass" data. A clear correlation was found between the two values, especially at altitudes below 2 km. A positive correlation is also seen in a scatter plot between ΔCO and ΔSO_x (Figure 7d). As for NO_y, the slope was lower than the emission ratio, E_{SO2}/E_{CO}, suggesting the removal of SO_x. Air masses sampled at 2-7 km appear to belong to two groups. In one of the groups, the slope of the increase is similar to that of the 0-2 km data, while very little increase of SO_x is found in the other group. These two groups of air masses were sampled during different flights (mostly from flights 13 and 19), however many of these air masses had been transported from below 800 hPa over the northeastern part of China. Consequently, the observed difference in the transport efficiency was largely due to differences in the transport processes, in which the degree of loss of SO_2 and/or $nssSO_4^{2-}$ was different.

5.3. Vertical Profile of $\varepsilon(NO_y)$

Average ΔCO and ΔNO_y values in "continental air mass" data were calculated within each altitude range (0-1, 1-2, 2-4, and 4-7 km), and the transport efficiency, $\varepsilon(NO_y)$, was calculated using these averages ($\overline{\Delta NO_y}$ and $\overline{\Delta CO}$). In this calculation, we only used data with $\Delta CO > 30$ ppbv. We took the ratio of the average rather than

using the median value of individual ratios because events in which ΔCO and ΔNO_y were large should have a greater impact on the overall efficiency of the transport. It has been reported that the majority of transport of pollutants from the Asian continent to the Pacific Ocean is generally the result of episodic events rather than continuous steady flow [*Bey et al*., 2001; *Jaffe et al*., 1999]. We note that the choice of the threshold value of ΔCO (> 30 ppbv) is not very sensitive to the results because the averages are used instead of using the medians.

A vertical profile of the average transport efficiency in the "continental air" is shown in Figure 8a (Table 3). In this figure, the transport efficiency calculated using only "Chinese air masses" is also shown. "Chinese air masses" were those that passed over China at altitudes below the 800-hPa level (boundary layer) within 5 days prior to measurement without passing over South Korea or Japan at these low altitudes, as described in section 3.1. We note that when air masses in which ΔCO > 30 ppbv are selected, Chinese air masses in each altitude range consist of 20-70% of the continental air masses. As seen in Figure 8a, a transport efficiency of 20-40% was found at 0-2 km. "Chinese air masses" at 0-2 km were mostly sampled over the Yellow Sea, and they were sampled within 24 hours after they had left the coast of China. The efficiency estimated in this study indicates that 60-80% of NO_y had already been removed in the source region before these air masses left the continent, although additional loss could have also occurred during this short transport over the ocean. The efficiency tends to be lower at higher altitudes, and values of about 15% were found at 2-7 km. The lower efficiency in the free troposphere suggests that HNO_3 and NO_3^- were removed by wet deposition during the vertical transport, because precipitation is often accompanied by convection and synoptic-scale air mass lifting along isentropic surfaces in association with cold frontal systems, which is known as the warm conveyer belt (WCB). The removal process is examined more quantitatively below.

In Figure 9a, vertical profiles of median values of HNO_3/NO_y and NO_3^-/NO_y in "continental air masses" are shown. These values are also given in Table 4. For this calculation, we only used data with $\Delta CO > 30$ ppbv. As seen in this figure, $HNO_3 + NO_3^-$ accounts for 50% and 30% of NO_y at 0-1 and 1-2 km, respectively. Henry's law equilibrium and laboratory studies of HNO_3 uptake on ice surfaces indicate that HNO_3 is ~100% fractionated into the condensed phase in both warm and glaciated clouds [*Mari et al*., 2000 and references therein]. One-dimensional model calculations for tropical continental deep convection suggest that about 80% of HNO_3 was scavenged during vertical transport [*Mari et al*., 2000]. Similarly, very low NO_3^-/NO_y values of 0.007 in the free troposphere, as compared with those observed in the boundary layer of 0.1-0.4, indicate that nitrate aerosols were also scavenged quite efficiently during vertical transport. In fact, ammonium nitrate (NH_4NO_3), which is generally seen in accumulation mode aerosol and which is considered to have been measured by the NO_y instrument, is expected to be efficiently scavenged by cloud droplets. Assuming 100% removal of HNO_3 and NO_3^- aerosols in the boundary layer during vertical transport into the free troposphere, the factor of 2 reduction of $\varepsilon(NO_y)$ estimated in this study can be explained. Formation of HNO_3 from NO_x during and after vertical transport retains the HNO_3/NO_y ratios in the free troposphere, while very low NO_3^-/NO_y ratios in the free troposphere suggest that the formation of nitrate aerosol was likely limited because an insufficient amount of NH_3 was available to neutralize the acidity.

The transport efficiency of NO_y during the TRACE-P period was also studied by *Miyazaki et al*. [this issue]. Although a single value was used for the background levels of NO_y and CO in their analysis, generally similar results were obtained: 30% and 10-20% in the boundary layer and free troposphere, respectively. Synoptic-scale WCB and convection were found to be important mechanisms for the transport of anthropogenic reactive nitrogen to the free troposphere. The transport efficiency of NO_y from North America was studied by *Stohl et al.* [2002] using North Atlantic

Regional Experiment (NARE) 1996 and 1997 data. They used CO and Lagrangian tracers as a reference and found that only 3-5% of NO_y emissions reached altitudes above 3 km. *Parrish et al*. [2002] also studied the relationship between NO_y and CO using five field campaigns and the NO_y transport efficiencies in the free troposphere are estimated to have been 18-27% and 9-11% for the experiments over the North America (summer season) and the western North Atlantic Ocean (spring and fall), respectively.

Vertical profiles of the partitioning of reactive nitrogen (Figure 9a and Table 4) show that PAN was the dominant species in "continental air masses" ($\Delta CO > 30$ ppbv). Because of the long lifetime of PAN at low temperatures in the free troposphere, PAN would be transported farther downwind and eventually produce NO_x after descending to lower altitudes. Consequently, this fraction is considered as a potential production of NO_x. Direct transport of NO_x, however, was found to be very limited. The NO_x/NO_y ratio was 0.06-0.12 and 0.02-0.05 at 0-2 km and 2-7 km, respectively (Figure 9a and Table 4). When $\varepsilon(NO_y)$ values in Table 3 (Figure 8a) are used, the transport efficiency of NO_x, $\varepsilon(NO_x)$, was calculated to be about 1-5% and 0.5% in the boundary layer and free troposphere, respectively. This result means that only 0.5% of anthropogenically emitted NO_x remained in the form of NO_x when these air masses were transported into the free troposphere. Values of NO_3^-/NO_y have large variability at 0-2 km, partly because the NO_3^- amount in aerosol is generally limited by the availability of NH_3. When median values of NO_3^-/NO_y are used, the formation efficiency of NO_3^-, $\varepsilon(NO_3^-)$, was calculated to be 3-16% and 0.1% in the boundary layer and free troposphere, respectively. This low yield in the free troposphere is due to the efficient scavenging of nitrate aerosol, as described above.

A scatter plot between $\varepsilon(NO_y)$ and NO_x/NO_y is shown in Figure 10a. As seen in this figure, these data show a positive correlation. Part of the correlation is due to vertical profiles of two quantities, however a correlation is seen even within the boundary layer data. Because the loss of HNO_3 and NO_3^- results in a higher NO_x/NO_y

ratio, a positive correlation cannot be simply explained by this process. When an air mass remained or stagnated within the boundary layer for a longer time period, conversion from NO_x to HNO_3 by gas-phase reaction with OH and nighttime heterogeneous reaction through N_2O_5 proceed further, leading to a lower NO_x/NO_y ratio. Concurrently, the loss of HNO_3 and NO_3^- results in a lower $\varepsilon(NO_y)$. Furthermore, during vertical transport, we may expect an efficient conversion of NO_x to HNO_3 due to the relatively large amounts of OH from H_2O and wet surface area for heterogeneous reaction. The results presented in this study suggest that the transport efficiency was higher in air masses that spent less time in the boundary layer, though a very limited fraction of emitted NO_x can still be brought into the free troposphere.

5.4. Vertical Profile of $\varepsilon(SO_x)$

Vertical profiles of the average transport efficiency of SO_x (=SO_2 + $nssSO_4^{2-}$), $\varepsilon(SO_x)$, in the "continental air masses" and "Chinese air masses" are shown in Figure 8b (Table 5). As for $\varepsilon(NO_y)$, averages of ΔSO_x and ΔCO in high-ΔCO air masses (ΔCO > 30 ppbv) were calculated ($\overline{\Delta SO_x}$ and $\overline{\Delta CO}$), and their ratio was divided by the emission ratio given in Table 2. As a result, the transport efficiency at 0-2 km was estimated to be 25-45%. "Chinese air masses" at 0-2 km were mostly sampled over the Yellow Sea, and they were sampled within 24 hours after they had left the coast of China, as described above. The efficiency estimated in this study indicates that 55-75% of SO_x had already been removed in the source region before these air masses left the continent. The transport efficiency of 15% at 2-7 km is lower than that at 0-2 km, suggesting that SO_2 and $nssSO_4^{2-}$ were removed by wet deposition during vertical transport. One-dimensional model calculations for tropical continental deep convection suggest that about 30% of SO_2 was scavenged during vertical transport [*Mari et al*., 2000]. Although this value is lower compared to the value of 80% for HNO_3 due to the low Henry's Law constant, $nssSO_4^{2-}$ particles are considered to have

been scavenged quite efficiently within the cloud and precipitation leading to lower $\varepsilon(SO_x)$ values in the free troposphere.

A vertical profile of median values of $nssSO_4^{2-}/SO_x$ ratio is shown in Figure 9b (and Table 4). At 0-1 km altitude, $nssSO_4^{2-}/SO_x$ ratios of about 0.6 were observed during each of the four fights, suggesting that the conversion from SO_2 to SO_4^{2-} had taken place quite efficiently near the source region. Ratios of $nssSO_4^{2-}/SO_x$ of about 0.3-0.7 were obtained from the ground-based measurements at Cheju Island in the East China Sea [*Carmichael et al*., 1997] and Taean station in Korea facing the Yellow Sea [*Kim et al*., 2001], which also suggest rapid conversion within the boundary layer. On the other hand, at 2-4 km, $nssSO_4^{2-}/SO_x$ ratios differ significantly between the flights. In air masses sampled over Japan during flight 19, $nssSO_4^{2-}$/SOx was quite low (Figure 9b), while the $\varepsilon(SO_x)$ values were higher than those of the other flights. During this flight, the CO, SO_2, and NO_y values reached 300-400 ppbv, 5-9 ppbv, and 2-4 ppbv, respectively, at 3 km, suggesting a significant impact from anthropogenic emissions. Because $\varepsilon(SO_x)$ values at 2-4 km during this flight were close to those at 0-1 km, the observed low $nssSO_4^{2-}/SO_x$ ratios might have been due to a limited formation of $nssSO_4^{2}$ particles, rather than the removal of $nssSO_4^{2-}$ particles. When a median value of $nssSO_4^{2-}/SO_x$ is used with the transport efficiency of SO_x, a formation efficiency of sulfate aerosol is estimated to be 10-25% and 2-9% at 0-2 km and 4-7 km, respectively. The efficiency in the free troposphere was higher than that of nitrate aerosol in the same altitude rage ($\varepsilon(NO_3^-) = 0.1\%$) likely because sulfate aerosols can be formed more easily in the free troposphere after removal during vertical transport.

A scatter plot of the transport efficiencies for NO_y and SO_x is shown in Figure 10b. As seen in this figure, they are positively correlated, even within each altitude range. This result suggests that loss processes of NO_y and SO_x proceeded simultaneously.

5.5. Comparison with $\varepsilon(NO_y)$ and $\varepsilon(SOx)$ Values Derived from DC-8 Data

In this study, the P-3B aircraft data were used exclusively. However, because measurements of NO_x, PAN, HNO_3, SO_2, and SO_4^{2-} (particles with diameters smaller than 2.7 μm) were also made onboard the NASA/DC-8 during TRACE-P, we performed the same analyses using the DC-8 data set obtained in the study area defined for the present study (30°N-42°N and 124°E-140°E). For NO_y values, we summed the DC-8 observations of NO_x, PAN, and HNO_3. In HNO_3 measurements, particulate nitrate of diameters smaller than 1-2 μm is considered to have been measured with gas phase HNO_3. When we plot a CO-CO_2 scatter plot using Halon 1211 and OCS as a color code, very similar results to those shown in Figures 6a-6c are obtained (not shown). The "background relationship" derived from the P-3B also fits the DC-8 data set well. This is partly because the same research group made measurements onboard the two aircraft for CO, CO_2, and species obtained from whole air sampling. In fact, very good agreement between the two sets of measurements was found during the P-3B/DC-8 intercomparison flights [*Eisele et al*, this issue].

Vertical profiles of $\varepsilon(NO_y)$ and $\varepsilon(SO_x)$ values derived from DC-8 "continental air" and "Chinese air" are shown in Figures 8a and 8b, together with the P-3B results. DC-8 "Chinese air masses" were selected using the same definition as that for P-3B data using air mass trajectories. These results are also summarized in Tables 3 and 5. As seen in the figure, the results obtained from measurements from the two aircraft agreed to within 50%. When only the transport efficiencies of SO_2 are compared, a similar degree of agreement was found at 0-2 km, although the P-3B values in the boundary layer and free troposphere were found to be lower and higher, respectively. Disagreement by a factor of 3 was found between the P-3B and DC-8 SO_2 measurements during the P-3B/DC-8 intercomparison flights [*Eisele et al*., this issue]. However, the agreement in the estimates indicates that the results obtained in this study are robust. Although data above 7 km were also used for the DC-8 statistics, the agreement with the DC-8 estimates derived using a greater number of data supports the

validity of the results obtained from the P-3B data at 4-7 km.

5.6. Budget and Export Flux

The transport efficiencies $\varepsilon(NO_y)$ and $\varepsilon(SO_x)$, defined in equations (1) and (2), were determined as a local quantity. The value of $\varepsilon(NO_y)$ was derived from the number density of observed NO_y in one air mass divided by the expected NO_y number density in that air mass assuming that there is no loss after anthropogenic input. Consequently, the efficiency can be 100% in individual air masses. On the other hand, the budget of NO_y and SO_x in the East Asia region has been estimated in various numerical model studies [e.g. *Bey et al*., 2001; *Chin et al*., 2000; *Tan et al*., 2002]. Usually, the export flux from a selected domain is calculated from the difference between the total source and total sink. The export flux fraction can be determined as the export flux divided by the total source of a selected domain. To compare the TRACE-P results with these estimates, we examined the export flux across the 130°E meridional plane at 30°N-40°N during the TRACE-P period. We determined the export flux fraction of NO_y as follows.

$$f(NO_y) = \frac{\int_z^{z+\Delta Z} F_{air} \cdot \overline{\Delta NO_y} \cdot \gamma \cdot dz}{(E_{NOx} / E_{CO}) \cdot \int_0^{tropopause} F_{air} \cdot \overline{\Delta CO} \cdot \gamma \cdot dz} \qquad (3)$$

where F_{air} is the eastward flux of air molecules and γ is the occurrence frequency of the events in which ΔCO > 30 ppbv were observed from the P-3B aircraft. The denominator is the expected total flux of NO_y molecules that could have crossed the meridional plane, assuming that there is no loss after receiving anthropogenic emissions. The numerator is the observed flux of NO_y molecules that actually crossed the meridional plane within each altitude range. The former is considered to correspond to the source strength of NO_y when we assume a homogeneous flux along the latitude

circle. Although we ignored transport taking place at altitudes above 7 km in our calculation, its contribution is considered small. For the calculation of the eastward flux of air molecules (a product of the air density and zonal wind speed), we used ECMWF data at the 130°E meridional plane at 30°N-40°N for the period when measurements in the study area were made. For $\overline{\Delta CO}$ and $\overline{\Delta NO_y}$ values, averaged values in the continental air masses shown in Figure 8a (Table 3) were used.

Using equation (3), the export flux fraction of NO_y at 0-7 km during TRACE-P was estimated to be 18%; 8% and 10% were through the boundary layer (0-2 km) and free troposphere (2-7 km), respectively. This result suggests that of total number of NO_x molecules emitted over the northeastern part of China, only 18% were transported out from the Asian continent into the western Pacific. About half of the export flux took place through the boundary layer and the other half took place through the free troposphere. The flux in the free troposphere is important for long-range transport, due to greater wind speeds and less-frequent removal, while the flux in the boundary layer suggests an impact on neighboring countries, such as Japan. Because our estimate was derived from a very limited number of observations, the results might not represent the whole budget of NO_y over East Asia. In particular, the occurrence frequency of pollution transport events (events in which $\Delta CO > 30$ ppbv) is highly dependent on where and when P-3B aircraft measurements were made, although only the relative frequency among the various altitude ranges was used for our estimation. Nevertheless, the method in the present study is useful because it provides an independent budget estimate without using model calculations. *Bey et al*. [2001] showed using the GEOS-CHEM model for the PEM-West B period (February-March 1994) that about 70-80% of NO_x emitted in Asia was lost within the domain by deposition of HNO_3, and the net export flux was 20-30%, although the contribution from biomass burning in the southern part of China was also included in their model calculations.

The export flux fraction of SO_x during TRACE-P at 0-7 km, 0-2 km, and 2-7 km was estimated to be 22%, 10%, and 12%, respectively. *Chin et al*. [2000] showed using the GOCART model that the export flux fraction of anthropogenic SO_x from eastern Asia was about 16%, with 2/3 of it as SO_2. Nearly half of the emitted SO_2 is lost by dry-deposition to the surface. *Tan et al*. [2002] showed using their 3D model calculations for the late winter/early spring period that about 50% of the anthropogenic SO_x emitted over East Asia was removed from the continental source regions. About 30% is further removed within the neighboring ocean (region west of about 155°E), and 20% is exported out of their model domain. The vast majority of the exported SO_x was in the form of sulfate aerosol.

Finally, we note that when considering the total export of CO (denominator of equation (3)), 30% was exported through the boundary layer and 70% was transported through the free troposphere. Although the size of the ΔCO value was similar at altitudes below 4 km, higher wind speeds resulted in a greater flux in the free troposphere. The CO flux within each 1-km layer was suggested to be greatest in the 2-4-km altitude range. This result is consistent with the model estimates of *Bey et al*. [2001]. The contribution of the export flux of NO_y and SO_x in the free troposphere was about half of the total, as described above. This fraction was lower as compared with that of CO, because loss during the vertical transport resulted in lower $\varepsilon(NO_y)$ and $\varepsilon(SO_x)$ values.

5.7. Uncertainties

Uncertainties in the estimation of transport efficiency are affected by uncertainties in the emission data, biogenic sources of CO_2 [*Vay et al*., this issue] which is not considered in this study, measurements imperfections, background relationships, the choice of the threshold value of ΔCO (30 ppbv), and loss of NO_y and SO_x in background air masses. Also, the two assumptions were made in our analyses: first,

CO, CO_2, NO_y, and SO_x values in background air masses have a linear relationship, and second, the ratio of enhancements due to anthropogenic emissions is always the same. It is hard to evaluate individual uncertainties in a consistent manner, however we estimated an overall uncertainty in our estimation of transport efficiency to be on the order of 50% (horizontal bars in Figures 8a and 8b).

Some specific sources of uncertainty are described here. First, *Palmer et al*. [this issue] shows using an inverse model analysis that the anthropogenic emissions of CO in China estimated by *Streets et al*. [this issue] is likely to be underestimated by 30%. When CO emissions are increased by 30% in our analyses, the transport efficiencies and the export flux fractions (eq. (3)) increase by about 30%.

Second, emissions from Japan and South Korea are examined. Emission ratios of CO, CO_2, and NO_x in Japan and South Korea are very different from those in China: E_{NOx}/E_{CO} is larger, while E_{CO}/E_{CO2} is smaller. The value of E_{SO2}/E_{CO2} in South Korea is also larger than that in China. Consequently, when an air mass is influenced by emissions over South Korea or Japan, the ratio of increase, $\Delta NO_y/\Delta CO$ and $\Delta SO_x/\Delta CO$, will be different from those expected from Chinese emissions. However, as shown in Figures 8a and 8b, results obtained using "continental air masses" generally agreed with those using "Chinese air masses". As explained in section 3.1, a more-strict criterion on the air mass trajectories was applied to select "Chinese air masses," suggesting the robustness of the current estimates.

Third, in situ sources of reactive nitrogen, lightning NO production and aircraft emissions, are examined. Lightning during the TRACE-P period was limited over India and Southeast Asia to latitudes lower than 30°N [*Fuelberg et al*., this issue], and their contributions to the budget of reactive nitrogen in the present study area are therefore considered small. Influences from aircraft emissions are also considered to be small at altitudes below 7 km [e.g., *Koike et al*., 2000]. Mixing of stratospheric air mass can increase ΔNO_y values, however results obtained using "Chinese air masses"

(originated from below the 800-hPa level) are considered to have been influenced little.

Fourth, transport of NO_y and SO_x in coarse mode particles is examined. As described in section 2, particulate matter with diameters greater than about 1 μm was not sampled either by aerosol composition measurement (PILS) or the NO_y measurement. It has been reported, however, that a significant amount of nitrate was contained in coarse mode aerosols sampled over the western Pacific [e.g. *Chen et al*., 1997; *Kim and Park* 2001]. If nitrate in these particles originated from anthropogenic NO_x emission, we have underestimated the total transport amount. Three-dimensional model calculations for the East Asia region for March 1994 period also suggest that, in the presence of mineral dust particles and sea-salt aerosols, a significant amount of HNO_3 is partitioned onto these particles, because carbonate in the dust particles and chloride in sea-salt aerosols are volatile and easily replaced by nitrate [*Song and Carmichael*, 2001]. During TRACE-P, coarse mode particles were also collected from the DC-8 [*Dibb et al*., this issue]. Analyses using these aerosol data indicate that air masses with elevated levels of dust particles (high $nssCa^{2+}$ levels) are generally mixed with pollutants because these air masses often passed over the northeastern part of China [*Jordan et al*., this issue]. As a result of an efficient uptake of HNO_3 by the dust particles, particulate NO_3^- constituted 50% of the total NO_3^- (gas phase HNO_3 + particulate NO_3^-) on average in these air masses [*Jordan et al*., this issue; *Dibb et al*., this issue]. Because HNO_3 constitute 10-20% of NO_y (Figure 9a and Table 4), we could have underestimated the transport efficiency of NO_y by 10-20% (upper limit). Chemical conversion of SO_2 to sulfate on mineral dust particles may also take place [*Xiao et al*., 1997]. Ground based measurements indicate that although most of the sulfate has been found on accumulation mode particles [*Chen et al*., 1997], significant amounts were found in the coarse mode during heavy dust events [*Kim and Park* 2001]. Though no major dust events occurred during TRACE-P, some signatures of uptake of SO_2 on dust particles were found from the DC-8 measurements [*Jordan et al*., this

issue]. More studies are needed in order for us to better understand the budget of nitrate and sulfate over East Asia.

Finally, the approach using a single background value is examined, because it has been used in various studies [e.g. *Parrish et al*., 1991; *Stohl et al*., 2002; *Miyazaki et al*., this issue]. When we use background values of CO and NO_y of 129 ppbv and 157 pptv, which are the minimum values at 0-2 km in the study area, a transport efficiency of NO_y for air masses used for the present study ($\Delta CO > 30$ ppbv in "continental air masses") at 0-2 km and 2-7 km is estimated to be 25-35% and 20%, respectively. This is well within the uncertainties in our estimate. Because the variability of the CO was large, the choice of a background CO level was not very critical during TRACE-P. However, if we use CO_2 as a reference, an error in the estimate will be large. This is because changes in CO_2 due to anthropogenic emissions were generally comparable to those caused by background air mass mixing.

6. Summary

The transport efficiencies of NO_y and SO_x ($\varepsilon(NO_y)$ and $\varepsilon(SO_x)$) were estimated using NASA P-3B and DC-8 data obtained during the TRACE-P experiment, conducted over the western Pacific between February and April 2001. Transport efficiency was defined as the observed NO_y (SO_x) number density in one air mass divided by the expected number density in that air mass assuming that there is no loss after receiving anthropogenic emission (equations (1) and (2)). For this purpose, we introduced a new method to estimate the background levels of various species in individual air masses that have experienced multiple injection, mixing, and loss processes. In this method, a linear relationship between CO and CO_2 in background air masses was used instead of using a single value of CO or CO_2. When CO and CO_2 are higher than this background relationship, levels of Halon 1211 and OCS, which are considered to be unique tracers of emissions from China, are also higher, suggesting the validity of our approach. We then estimated an increase of CO, NO_y, and SO_x in individual air masses (ΔCO, ΔNO_y, and ΔSO_x), and the transport efficiencies were calculated using CO as a passive tracer.

We selected the study area of 30°N-42°N and 124°E-140°E because air masses sampled in this area had mostly been transported from over the northeastern part of China and had very little effects from a volcano on Miyakejima Island. Air masses sampled in the study area were denoted as “continental air masses” in this study. In addition, we defined “Chinese air masses” that passed over China at altitudes below the 800-hPa level (boundary layer) within 5 days prior to measurements without passing over South Korea or Japan at these low altitudes. “Chinese air” is a sub-set of “continental air.” Emission inventory data showed a good correlation between emissions of CO, CO_2, NO_x, and SO_2 over the northeastern part of China (25°N-50°N and 100°E-130°E, except for South Korea region) where “continental air masses” had generally originated. This result indicates that various emission sources are generally

co-located and ensure that the use of single emission ratios in our study, E_{CO}/E_{CO2}, E_{NOx}/E_{CO}, and E_{SO2}/E_{CO}, is reasonable.

Averages of ΔCO, ΔNO_y, and ΔSO_x values were calculated for air masses in which $\Delta CO > 30$ ppbv in "continental air masses," and the transport efficiencies were calculated by taking their ratios. Vertical profiles of the transport efficiencies in "continental air masses" generally agreed with those in "Chinese air masses," within the uncertainties (50%). The results from the P-3B showed that 20-40% and 15% of NO_x emitted over the northeastern part of China remained as NO_y at 0-2 km (boundary layer) and 2-7 km (free troposphere), respectively. PAN was found to be the dominant form, while only 0.5% of emitted NO_x remained as NO_x in the free troposphere. The transport efficiency of SO_x was estimated to be 25-45% and 15-20% in the boundary layer and free troposphere, respectively. Median values of SO_4^{2-}/SO_x ratio were 0.4-0.6 both in the boundary layer and free troposphere, though large variability was found in the free troposphere. These estimates were generally consistent with those derived using DC-8 data. The results obtained in this study indicate that more than half of NO_y and SO_x were lost over the continent and that the vertical transport from the boundary layer to the free troposphere further reduced their amounts by a factor of 2. Because $HNO_3+NO_3^-$ consisted of about 50% of NO_y at 0-1 km, a very efficient wet removal of these two compounds during the vertical transport was suggested to be responsible for the observed reduction in NO_y. Furthermore, a positive correlation between the transport efficiencies of NO_y and SO_x indicates that the loss processes of these two species likely proceeded simultaneously. In general, the transport efficiency has been estimated well, however relatively large uncertainties remain in the processes controlling the gas to particle conversion.

The export flux fraction was defined as the flux of observed NO_y (SO_x) molecules in each altitude range divided by the expected total flux (surface to the tropopause) of NO_y (SO_x) molecules assuming that there is no loss after receiving anthropogenic

emission (equation (3)). As a result, export flux fractions of NO_y at 0-7 km, 0-2 km, and 2-7 km were estimated to be 18%, 8%, and 10%, respectively. The export flux fractions of SO_x in these three altitude ranges were estimated to be 22%, 10%, and 12%, respectively. These results indicate that the total flux of NO_y and SO_x from the continent was estimated to be 20% of the total emissions over the northeastern part of China. Flux in the boundary layer and free troposphere was found to have a similar contribution. This relative contribution in the free troposphere was lower as compared with that of CO because of the wet removal during the vertical transport.

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Figure Captions

Figure 1. Flight tracks of the NASA/P-3B during TRACE-P. Locations where "continental air masses" and "Chinese air masses" were sampled are also shown. "Continental air masses" are those sampled at 30°N-42°N and 124°E-140°E (excluding air masses that could have been influenced by a volcano on Miyakejima Island). "Chinese air masses" are a sub-set of "continental air masses" and are those passed over China at altitudes below the 800-hPa level (boundary layer) within 5 days prior to measurement without passing over South Korea or Japan at these low altitudes. Locations where air masses in which $\Delta CO > 30$ ppbv were sampled (signature of influences from anthropogenic emissions) are also shown.

Figure 2. Distribution of anthropogenic emissions of (a) CO, (b) CO_2, (c) NO_x, and (d) SO_2 for the year 2000 at 1° × 1° resolution [*Streets et al*., 2002]. To distinguish high-emission areas, only areas in which emissions are higher than certain criteria (CO > 3 Gmol/yr, CO_2 > 70 Gmol/yr, NO_x > 0.2 Gmol/yr, and SO_2 > 0.15 Gmol/yr) are plotted.

Figure 3. Scatter plot between anthropogenic emissions (1° × 1° gridded data) in the region of 25°N-50°N and 100°E-130°E, except for South Korea (30°N-38°N and 126°E-130°E). This region covers mainly industrial regions in the northeastern part of China. Ratios of total emission amounts in this region (Table 2) are also shown by solid lines. These ratios were used as E_{CO}/E_{CO2}, E_{NOx}/E_{CO}, and E_{SO2}/E_{CO} in the present analyses.

Figure 4. Schematic diagrams showing the procedure to derive background values (C) from observations (C' or C'').

Figure 5. Vertical profiles of CO, CO_2, NO_y, and SO_x (= SO_2+nssSO_4^{2-}). All of the P-3B data obtained at west of 155°E are used irrespective of the latitude (17°N-42°N) except for those possibly influenced by a volcano on Miyakejima Island. Potential temperature is used as the vertical coordinate. A solid line in

each figure is a polynomial fit calculated for minimum values at each potential temperature level and is referred to as "minimum value line" in the text.

Figure 6. Scatter plot between CO and CO_2 in "continental air masses," which were sampled at 30°N-42°N and 124°E-140°E (P-3B data). Color was coded using (a) sampling altitude, (b) Halon 1211 mixing ratio, and (c) OCS mixing ratio. Open squares show pairs of CO and CO_2 values on the "minimum value lines" shown in Figures 5a and 5b. A solid line is a least squares fit to these open squares, and it will be referred to as "background relationship" in the text. The dashed line denotes the emission ratio of CO relative to CO_2 (E_{CO}/E_{CO2}) in the northeastern part of China (Table 2).

Figure 7. Scatter plots between (a) NO_y and CO, (b) SO_x and CO, (c) ΔNO_y and ΔCO, and (d) ΔSO_x and ΔCO in "continental air masses" (P-3B data). ΔSO_x values are identical to SO_x values because a zero background was assumed. Open squares show pairs of NO_y and CO or SO_x and CO values on the "minimum value lines" shown in Figures 5a, 5c, and 5d. A solid line and dashed line denote the "background relationship" and the emission ratio (E_{NOx}/E_{CO} or E_{SOx}/E_{CO}) in the northeastern part of China (Table 2), respectively. Black squares denote air masses in which $\Delta CO < 30$ ppbv.

Figure 8. Vertical profiles of the transport efficiency for (a) NO_y, defined in eq. (1) and (b) SO_x (= SO_2+nssSO_4^{2-}), defined in eq. (2). Solid and dashed lines are the results for "continental air masses" and "Chinese air masses," respectively. Heavy and light lines are the results from the P-3B and DC-8, respectively. Values of ΔCO, ΔNO_y, and ΔSO_x were averaged (only using air masses in which $\Delta CO > 30$ ppbv) before taking their ratios. Emission ratios, given in Table 2 were used.

Figure 9. (a) Vertical profile of the partitioning within the NO_y species (P-3B data). Median values and 67% ranges (horizontal bars) in "continental air masses" (and

$\Delta CO > 30$ ppbv) are shown. (b) Vertical profile of $nssSO_4^{2-}/SO_x$ ratio (P-3B data). Median values and 67% ranges (horizontal bars) in "continental air masses" (and $\Delta CO > 30$ ppbv) are shown. Individual data points are also shown.

Figure 10. Scatter plot between (a) NO_x/NO_y and transport efficiency of NO_y, and (b) transport efficiencies of NO_y and SO_x (P-3B data). Air masses in which $\Delta CO > 30$ ppbv within "continental air masses" are used.

Table 1. Measurements onboard the NASA P-3B and DC-8 aircraft during TRACE-P

Species	Aircraft	Technique	Reference
CO	P-3B, DC-8	Differential absorption technique using a tunable diode laser	*Sachse et al*., 1987
CO_2	P-3B, DC-8	Non-dispersive infrared (NDIR) analyzers	*Vay et al*., 1999
NO, NO_2, NO_y	P-3B	Chemiluminescence / photolysis converter / gold catalytic converter	*Kondo et al*., 1997
NO, NO_2	DC-8	Two-photon laser-induced fluorescence (TP-LIF)	*Bradshaw et al*., 1999
PAN	P-3B	GC/ECD	
PAN	DC-8	GC/ECD	*Singh et al*., 1996
HNO_3	P-3B	CIMS	*Mauldin et al*., 1998
HNO_3	DC-8	Mist chamber / ion chromatography	*Talbot et al*., 1997
SO_2	P-3B	Atmospheric pressure ionization mass spectrometry (APIMS)	*Thornton et al*., 2002
SO_2	DC-8	Mist chamber / ion chromatography	
SO_4^{2-} and NO_3^-	P-3B	Particle-into-liquid sampler (PILS)	*Weber et al*., 2001
SO_4^{2-}	DC-8	Mist chamber / ion chromatography	*Scheuer et al*., 2002
NMHCs/ halocarbons	P-3B, DC-8	Whole air samples / GC / FID / ECD / MS	*Blake et al*., 2001

Table 2. Emission and emission ratio of CO, CO_2, NO_x, and SO_2 in the northeastern part of China (25°N-50°N & 100°E-130°E, except for South Korea)

	Amount (tera-mol/yr)	Ratio to CO (mol/mol)	Ratio to CO_2 (mol/kilo-mol)
CO	3.08	1	48.4
CO_2	63.7	20.7	1
NO_x	0.162	0.0527	2.55
SO_2	0.212	0.0690	3.33

Table 3. Transport efficiency of reactive nitrogen

	P-3B			DC-8
	$\varepsilon(NO_y)$	$\varepsilon(NO_x)$	$\varepsilon(NO_3^-)$	$\varepsilon(NO_y)$
4-7 km	0.18 (0.18)	0.004	0.001	0.14 (0.11)
2-4 km	0.13 (0.13)	0.007	0.001	0.13 (0.08)
1-2 km	0.21 (0.18)	0.013	0.025	0.26 (0.25)
0-1 km	0.38 (0.28)	0.048	0.16	0.31 (0.26)

Results are for air masses in which $\Delta CO > 30$ ppbv within "continental air masses." Values in parentheses are for "Chinese air masses."

Table 4. Partitioning within NO_y and SO_x (P-3B)

	NO_y				SO_x
	NO_x/NO_y	PAN/NO_y	HNO_3/NO_y	NO_3^-/NOy	$nssSO_4^{2-}/SO_x$
4-7 km	0.023	0.53	----------	0.0066	0.10
2-4 km	0.051 (0.028-0.078)	0.46 (0.36-0.64)	0.23 (0.12-0.33)	0.0078 (0.0015-0.0723)	0.49 (0.01-0.87)
1-2 km	0.064 (0.036-0.083)	0.39 (0.30-0.52)	0.17 (0.10-0.23)	0.12 (0.00-0.49)	0.37 (0.21-0.83)
0-1 km	0.12 (0.09-0.17)	0.34 (0.25-0.38)	0.091 (0.046-0.146)	0.42 (0.26-0.74)	0.56 (0.45-0.71)

Median values for air masses in which $\Delta CO > 30$ ppbv within "continental air masses." Values in parentheses are 67% ranges.

Table 5. Transport efficiency of SO_x

	P-3B		DC-8
	$\varepsilon(SO_x)$	$\varepsilon(nssSO_4^{2-})$	$\varepsilon(SO_x)$
4-7 km	0.15 (0.14)	0.015	0.06 (0.14)
2-4 km	0.18 (0.16)	0.087	0.14 (0.16)
1-2 km	0.27 (0.24)	0.10	0.38 (0.24)
0-1 km	0.45 (0.29)	0.25	0.43 (0.29)

Results are for air masses in which $\Delta CO > 30$ ppbv within "continental air masses." Values in parentheses are for "Chinese air masses."